

Effects of Water and Hydrogen Chloride on the Reaction of 1,1-Diphenylethylene with AlCl_3

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ABSTRACT

The reaction of 1,1-diphenylethylene with AlCl_3 in CH_2Cl_2 at low temperature in the presence of small amounts of water (present as residual impurity or deliberately added) occurs in two successive stages : a very rapid reaction cocatalysed by water and a slower one resulting from a direct (bimolecular) initiation. The stoichiometry of the reaction involving water has been determined : $3 \text{H}_2\text{O}$ and 6AlCl_3 are necessary to form 4 carbocations.

In the same conditions, hydrogen chloride has no influence either on the extent of the first stage or on the yield and the rate of the second stage.

INTRODUCTION

1,1 diphenylethylene (DPE) is a suitable monomer to study the mechanisms of initiation in cationic polymerizations. At low temperatures, the initiation by Lewis acids as well as by protonic acids is faster than the propagation which is limited to a dimerization. The carbocations are stable and the initiation rate may be derived from spectrophotometric measurements [1].

In a first investigation on the kinetics of initiation by aluminum chloride in dichloromethane, we found that the initiation could be divided in three successive stages [2]. The first one, very fast, was attributed to a cocatalytic reaction due to residual impurities. The second stage was assigned to a direct bimolecular reaction between the olefin and the metal halide and the third stage, much slower than the second, received only speculative interpretations : slow degassing of cocatalyst or slow initiation by AlCl_2R . As this stage has been also observed with the same rate in the case of TiCl_4 and $\text{CF}_3\text{SO}_3\text{H}$ initiators, its signification should be reexamined as will be done in a following paper.

We present now more detailed results on the cocatalytic effect of water and hydrogen chloride.

EXPERIMENTAL

1,1-diphenylethylene, dichloromethane and aluminum chloride

were purified and stored in sealed tubes equipped with break-seals [2].

Hydrogen chloride was dried over P_2O_5 and distributed in phials containing known amounts at pressure slightly lower than 1 atm. One phial was broken under vacuum above the $AlCl_3$ solution cooled at the experiment temperature. After a delay of some minutes in order to reach the vapour-solution equilibrium, a phial containing DPE immersed in the solution was broken to start the reaction.

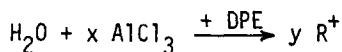
Solutions of water in CH_2Cl_2 were titrated by nmr and used to prepare phials of DPE solution which were broken inside the $AlCl_3$ solution, so introducing simultaneously monomer and cocatalyst.

RESULTS

Cocatalysis by water

Even in the most drastic conditions of purity, the initiation of DPE by $AlCl_3$ involved a first step, very fast, leading to $3.10^{-5} M.l^{-1}$ of carbocations, independently of the concentrations of reactants and of the temperature. This step, which could be reduced by working in a smaller apparatus, was assigned to a cocatalytic effect of residual impurities such as water adsorbed on the walls. Therefore, we examined in some detail the effect of added water on the extent of the first step. Water and DPE were mixed in the same phial so that they were introduced simultaneously into the $AlCl_3$ solution. The ratio of added water to $AlCl_3$ ranged from 0.24 to 0.95 (Table I and Fig. 1). In experiment 4, the fast step was complete in less than one minute and was not followed by a second one. Thus the ratio $|H_2O|/|AlCl_3|$ corresponded exactly to the stoichiometry of the cocatalysed reaction.

Let us write the reaction :



where $x = |AlCl_3|_0/|H_2O|_t$ and $y = |R^+|_I/|H_2O|_t$

$|R^+|_I$ is the concentration of carbocations formed during stage I and $|H_2O|_t = |H_2O|_{added} + 3.10^{-5}/y$, i.e. the sum of added water plus the residual water responsible for the formation of ca. $3.10^{-5} M$ of carbocations in the purest conditions. From experiment 4, y was found equal to 1.31 and $x = 2.05$.

In experiment 3, the ratio $|AlCl_3|_0/|H_2O|_t$ was higher than 2 and the cocatalysed reaction was followed by a slow reaction attributable to a direct initiation by $AlCl_3$ in excess (stage II). For this experiment y was equal to 1.36.

Table 1

COMPARISON OF THE INITIATION OF DPE IN THE PRESENCE AND IN THE ABSENCE OF WATER OR HCl.

Exp.	$ \text{DPE} \cdot 10^2$ (M)	$ \text{AlCl}_3 \cdot 10^4$ (M)	added cocat.	$ \text{Coc} \cdot 10^4$ (M)	$ \text{Coc} / \text{AlCl}_3 $	T°C	$ \text{R}^+ _I \cdot 10^4$ (M)	$ \text{R}^+ _\infty \cdot 10^4$ (M)	$k_1 \cdot 10^2$ (stage II)
1	6.0	4.85	none	0	0	-30	0.29	2.41	2.85
2	5.2	6.18	4.0 (HCl)	0.65	0.65	-30	0.19	3.20	2.00
3	6.0	5.15	1.25 (H ₂ O)	0.24	0.24	-30	2.00	2.67	
4	2.0	2.20	0.84 (H ₂ C)	0.38	0.38	-30	1.40	1.40 ^a	
5	3.65	2.28	1.30 (H ₂ O)	0.57	0.57	-30	1.40	1.88	
6	5.6	1.95	1.85 (H ₂ O)	0.95	0.95	-30	~1.35 ^b	0	
7	1.46	2.13	none	0	0	-60	0.10 ^c	1.13	0.13
8	3.34	5.70	14.3 (HCl)	2.50	2.50	-58	0.36	-	0.12

a) Value slowly decreasing with time.

b) Value extrapolated at zero time because of a rapid destruction.

c) Experiment carried out in a much smaller apparatus described in ref. 2.

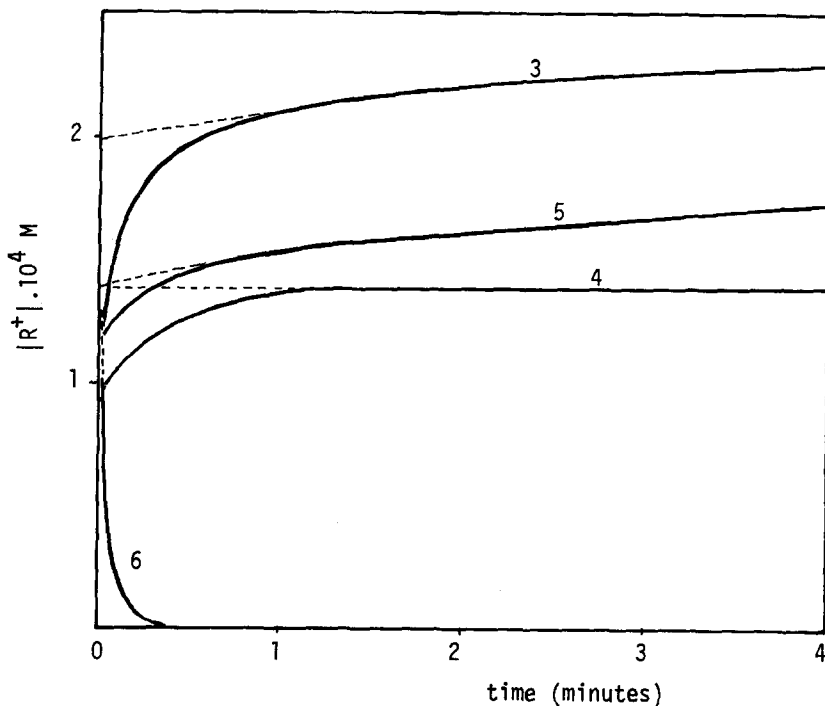
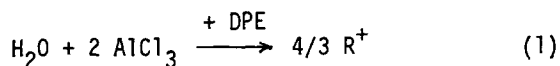


Fig. 1 : Kinetics of carbocation formation at -30° in the system DPE- AlCl_3 - H_2O - CH_2Cl_2 .

Figure 2 shows a plot of the number of carbocations formed in stage I per water molecule versus the ratio $[\text{AlCl}_3]_0/[\text{H}_2\text{O}]_+$. It is clear that this number of carbocations is directly proportional to AlCl_3 concentration when this one is lower than that required by the stoichiometry of the cocatalyzed reaction. On the contrary, it becomes independent of AlCl_3 when the ratio $[\text{AlCl}_3]_0/[\text{H}_2\text{O}]_+$ is higher than the stoichiometry ($x = 2$). Then 1.34 carbocations (i.e. $4/3$) are formed for each water molecule and the balance of the water-cocatalysed initiation may be written :



Thus more than one proton of water may be active in cocatalysis. A similar result has been previously observed in the case of TiCl_4 where 1.60 carbocations from DPE were formed per water molecule [3].

From the literature, it is known that a partial hydrolysis of AlCl_3 yields $\text{AlCl}_2(\text{OH})$ and $\text{AlCl}(\text{OH})_2$ [4]. On the other hand,

trialkylaluminum leads to tetraalkylaluminumoxane $R_2Al-O-AlR_2$ [5] and $TiCl_4$ in dioxane to $Cl_3Ti-O-TiCl_3$ [6]. A very interesting observation has been reported by Brown and Pearsall [7]. They found that, during hydrolysis of solid $AlCl_3$ by water in the vapour phase, hydrogen chloride evolved in the proportion of 1.4 moles per water mole, a value strikingly close to our value of 1.33 carbocations per water molecule.

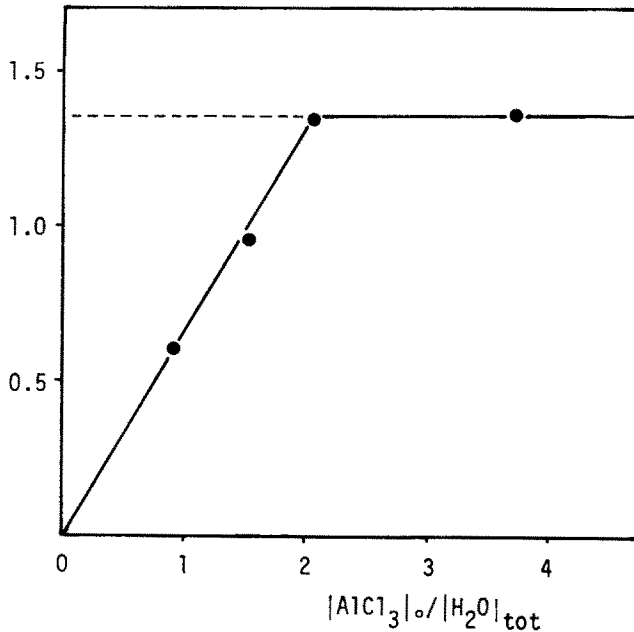
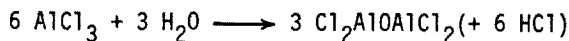
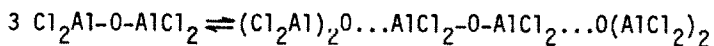


Fig. 2 : Relative yield of initially formed carbocations $|R^+|_Y / |H_2O|_{tot}$ as a function of the ratio $|AlCl_3|_0 / |H_2O|_{tot}$.

The simplest way to write the partial hydrolysis of $2AlCl_3$ by $1 H_2O$ is to form the corresponding tetrachloroaluminumoxane $Cl_2AlOAlCl_2$. In order to reconcile with equation (1), one may write :



However, 4 HCl only may become active since 4 R^+ are formed starting from 6 $AlCl_3$. One possible explanation would be that the tetrachloroaluminumoxane associate rapidly, giving aggregates with a lower number of empty orbitals, for example :



Such a species has only 4 free orbitals, and may complex

4 Cl^- , giving 4 active protons and then 4 carbocations.

In experiment 6, there was a large excess of water with respect to the stoichiometry and the carbocations formed were destroyed very rapidly (Fig. 1). In Experiment 5, with a smaller excess of water, the concentration of carbocations increased slowly after the end of stage I and finally reached a plateau. As AlCl_3 had been entirely consumed during stage I, the further increase of $4.8 \cdot 10^{-5} \text{ M}$ of carbocations could not be attributed to a direct initiation as in Experiment 1. It might be due to a slow reaction of water with the aluminoxane, the latter compound being still weakly active.

Effect of hydrogen chloride

Two experiments have been carried out in the presence of dry hydrogen chloride at -30° and -58° (Exp. 2 and 8, Table I). HCl in the vapour phase was introduced into a cold solution of AlCl_3 and a phial of DPE in CH_2Cl_2 was broken inside the solution. These experiments showed that HCl has almost no effect neither on the extent of the stage I nor on the yield and the rate in stage II. (the rate constants k_i have been calculated as previously [2]). In the experiment at -58° , HCl was used in excess, but the extent of the first stage $|\text{R}^+|_I = 3.6 \cdot 10^{-5} \text{ M}$ fell very well within the limits obtained in the absence of added cocatalyst (between 1.9 and $4 \cdot 10^{-5} \text{ M}$) in the same apparatus. The lower value $|\text{R}^+|_I = 1 \cdot 10^{-5} \text{ M}$ in the comparative experiment 7 is due to the use of a smaller apparatus (described in ref. 2).

Thus HCl added to AlCl_3 prior to monomer has no cocatalytic effect. Accordingly, the effect of water cannot be explained by a simple two-step process in which hydrolysis of AlCl_3 would produce HCl acting then as a coinitiator for AlCl_3 . One must assume a concerted mechanism involving the monomer, and also a coordination of HCl with a stronger electron acceptor.

Some conflicting results have been reported on the effect of HCl on polymerizations initiated by AlCl_3 . In the case of styrene, in CCl_4 solution, it is not a coinitiator [8] whereas it is a rate promoter in the case of isobutene [9]. On the other hand, we found that HCl was very active in the case of the system $\text{DPE-TiCl}_4\text{-CH}_2\text{Cl}_2$ [3]. The reason why it behaves differently in these systems is not clear. The difference between the AlCl_3 and TiCl_4 systems (at least in the case of DPE) might be due to a possible activation effect of HCl on an inactive complex of monomer and TiCl_4 , whereas AlCl_3 would not form such a complex and would react directly with the monomer.

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